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TAILORING THE INTERFACE IN GRAPHITE-
REINFORCED POLYCARBONATE

J. L. Kardos, et al

Monsanto Research Corporation

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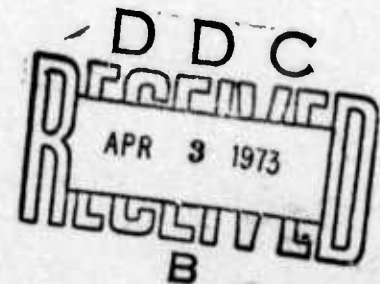Advanced Research Projects Agency

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FOREWORD

The research herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

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Pronounced effects of thermal treatment on the properties of graphite fiber/polycarbonate and glass fiber/polycarbonate composites have been demonstrated and explained. At 20 volume percent loading of random-in-a-plane, discontinuous fibers, both specimen strength and modulus in both fiber systems were found to increase dramatically upon molding above 260-265°C, whereas only the graphite system was further improved by subsequent annealing. In the latter case, property improvement is due to generation of a crystalline innerlayer at the interface, which apparently transfers the stresses more effectively from fiber to fiber. Regardless of the type of fiber, molding at 275°C (slightly above 260-265°C, the melting point of crystalline polycarbonate) results in improved properties due to better wetting of the fibers by the resin. Hot forming of graphite reinforced polycarbonate composites between the molding and annealing steps takes advantage of the higher processability of the unannealed material in addition to providing increased modulus and strength in the final molded article.

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INTRODUCTION

One of the more promising recent discoveries in composites research is that the structural properties of certain composites systems can be markedly changed through incorporation of a resin innerlayer between the matrix resin and the reinforcement. In contrast to the coupling agents often employed to improve the environmental resistance of FRP systems, these innerlayers may be up to several mils in thickness and vary in their effect depending on their own physical properties. Kenyon and Duffy (1) observed, for example, that the ultimate elongation of cast, glass bead filled epoxy composites can be increased simply by altering the nature of resin in the vicinity of the interface with an excess of glycidoxy silane. Kenyon (2) went on to show that the toughness of such systems also can be increased by coating the beads with a thin layer of flexibilized epoxy prior to casting. More recently, Lavengood and co-workers (3) found that the transverse strength and fatigue properties of fiber reinforced composites can be increased through use of a ductile innerlayer; in some cases, the improvement in fatigue life was as much as two orders of magnitude. Benefits were also seen in the axial flexural

properties of unidirectionally reinforced continuous and dis-
continuous fiber composites, but this was attributed more to
reduction of stresses at points of environmental corrosion
than to any other factor. In all cases, the effects on com-
posite properties were very sensitive to innerlayer thickness.

Little advantage has been taken of innerlayer or interface
effects in thermosetting composites because of the difficulty in
incorporating them into practical systems. However, several
workers have reported that innerlayers of the type required can
be readily generated in-situ in certain thermoplastic systems.
Baer et al., (4) demonstrated sometime ago that polymers could
be epitaxially crystallized from solutions and melts on hetero-
geneous surfaces to yield a layer of oriented crystallites. In-situ
crystallization of polyamides was observed by other workers at
about the same time (5,6). Lando and Frayer (7) reported epitaxial
crystallization of nylon 6 and 66 monomers on graphite surfaces
followed by topotactic reaction to yield layers of epitaxial
oligomer. Epitaxial crystallization of polyethylene on single
crystals of graphite has been demonstrated by Tuinstra and Baer (8).
While none of these workers were directly concerned with composites,
they nonetheless demonstrated that oriented crystallites could be
generated on heterogeneous substrates. In reinforced thermo-
plastic systems, this presents the possibility of producing an
innerlayer modulus intermediate between that of the substrate and
the bulk resin, a prime requirement for good stress transfer.

The so-called "high temperature" engineering thermoplastics' are particularly desireable as composite matrices because of their high toughness, heat stability and processability, in addition to good strength and stiffness characteristics. Many of this family also are amorphous in nature, or are at least very difficult to crystallize under usual processing and use conditions, and remain in the glassy state with little change in properties as long as they are held below Tg and protected from solvents. As indicated, some can be made to crystallize, however, and so have the potential for forming crystallite-rich innerlayers around reinforcing agents embedded in the resin. When crystallization does occur, the physical properties of the resin usually change greatly.

The morphology of a surprising number of these amorphous thermoplastics is strikingly similar. As indicated in Table I, these include polycarbonate, polyethylene terephthalate and polysulfone. In the "non-crystalline" state these materials have been found (9, 10) to consist of tiny ball-like structures of about 75Å in size. When the system is held at temperatures near Tg for long periods or is exposed to certain solvents, morphological changes begin to occur which involve gradual alignment of these structures to form lamellae and, subsequently, spherulites. Similar changes can be induced by strain crystallization. The

mechanisms of crystallization by annealing and straining are not fully understood but appear to be the same for all the systems exhibiting the ball-like morphology.

The key question in our study was whether or not these crystallization techniques could be applied to composite systems. The previously mentioned work of Lando and Frayer and Tuinstra and Baer suggested that graphite such as found in high modulus graphite fibers might be a suitable substrate for crystallization if the system was subjected to the proper conditions, e.g., long term annealing. If this were the case, it seemed likely that advantage could be taken of the property enhancement obtainable with innerlayers and that unusually high levels of composite performance could be achieved.

This paper concerns the application of these crystallization techniques in thermoplastic composite systems. Preliminary work (15) showed that graphite fiber could be used as nucleating sites for polycarbonate resin and that the properties of resulting composites were significantly improved. Completion of the study has verified the early findings and shown that thermal tailoring of the interface in thermoplastic composites is applicable to practical polymer processing.

FABRICATION OF COMPOSITES

Polycarbonate composites were prepared from five different types of reinforcement:

silane-treated glass spheres[1], carbospheres[2], heat cleaned 1/4"
glass fibers[3], 1/8" Thornel[4] 40 graphite fiber sized with poly-
vinyl alcohol and 1/8" HMG[5] graphite fibers sized with Epon 828[6].
Loading was 20% by volume in all cases. The reinforcements were
chosen to permit differentiation between simple wetting of the
surface by the resin and development of a partially crystallized
layer of resin bonded to the surface. In addition, these
materials permitted comparison of the degree of reinforcement
obtainable with spheres versus short fibers and with fibers of
varying stiffness. Fiber properties ranged from a nominal strength
and elastic modulus for the glass fiber of 300×10^3 psi and
10.6×10^6 psi to those of Thornel 40, 200×10^3 psi and 36.5×10^6
psi, to those of the HMG fiber, 300×10^3 psi and 56×10^6 psi,
respectively.

The sphere-containing composites were prepared by dry blending
40 mesh vacuum dried polycarbonate powder with "cleaned" spheres
and then molding under positive pressure. Cleaning of the glass
spheres was accomplished by removal of metallic particle contaminates
with a magnet, slurrying them in an equal weight of acetone con-
taining 5 w/o A-1100[7] silane and then filtering and drying

---

1. Soda-lime glass spheres averaging 40 microns in diameter pro-
duced by the Microbeads Division of Cataphote Corp. 2. Hollow,
thin-walled carbon spheres, averaging 40 microns in diameter,
trade-marked by the General Techniologies Corp. 3. Type CS-250
produced by Johns Manville Fiber Glass Inc.; sizing removed at
600°C. 4. Trademark of Union Carbide Corp. 5. Trademark of
Hercules Powder Co., Inc. 6. Trademark of Shell Chemical Co.
7. Trademark of Union Carbide Corp.

them under vacuum at 110°C. The carbon spheres were simply freed
of broken sphere fragments by floatation in methanol and dried
under vacuum at 110°C. Apparent density of the latter was deter-
mined to be 0.475 g/cc by casting them in epoxy resin, care being
taken to exclude voids, measuring composite density with a water
pycnometer and determining the sphere weight content in the com-
posite by the method of Haynes and Tolbert (16). Direct measure-
ment of Carbosphere apparent density using a Beckman Model 930
Air Comparison Pycnometer gave a value of 0.5g/cc; this is con-
sidered to be slightly in error but to provide a valid upper
limit. Molding of the polymer/sphere blends was carried out under
the same conditions used to mold unfilled specimens from poly-
carbonate powder alone. Specimens were prepared by heating the
resin mix to molding temperature under low contact pressure,
followed by (1) holding at 190°C for 10 minutes under 1000 psi
before cooling to room temperature, (2) holding at 275°C for 10
minutes under 100 psi, then cooling to 200°C and increasing
the pressure to 1000 psi for the remainder of the cool down
period or (3) holding at 275°C for 10 minutes under 50 psi,
annealing at 245°C for 10 minutes under 50 psi and then annealing
at 245°C for 3 hours before cooling to 200°C and increasing the
pressure to 1000 psi for cool down. The pressure cycles were
chosen to prevent excessive flashing of the resin and formation
of voids and to provide uniform thickness in all specimens. A
minimum of four tensile specimens of each material and the un-
filled resin were prepared for each molding condition.

The fiber reinforced specimens were prepared by sonically dispersing the appropriate fiber in a 75% methanol/25% water solution along with 60-100 mesh polycarbonate powder. A preform mat of fibers, random in two dimensions and uniformly mixed with resin power, was then prepared from the suspension by draining off the solution through a filter shaped like the final sample (5 x 1/2 x 1/16 in. plate) in the bottom of the container. The mat was dried at 110°C for 8 hr. under vacuum and compression molded at 5000 psi using the following temperature cycles. The fiber/resin mixture was heated under pressure to 190°C, held for 10 min. and slowly cooled to room temperature; to 275°C, held for 10 min. and cooled; or to 275°C, held for 10 min. and annealed for 3 hr. at 245°C before cooling. A total of 12 specimens was prepared under each regime and an equal number of unfilled bars of the same geometry and molded under the same conditions were prepared as standards.

The temperature cycles employed for the moldings were chosen to permit differentiation of effects occuring (1) under normal molding conditions (190°C) for the pure resin, (2) when the melting point (265°C) of the resin was exceeded (275°C), (3) when the development of crystallites in a layer of resin at the resin/reinforcement interface was most favored (annealing at 245°C after melting. Selection of 245°C as the annealing temperature was based on earlier observations indicating that this was the point (about 20° below Tm) of most rapid crystal growth.

RESULTS AND DISCUSSION

Composite Properties

The tensile properties and glass transition temperatures of the various composites which were prepared are shown in Tables II and III. In all cases, there was an observable effect of the thermal treatments on mechanical properties. In the sphere-reinforced systems the effect was largely deleterious, particularly in the case of annealing which caused marked decreases in the already low elongations of the filled materials.

Effects in the fiber-reinforced systems were beneficial, however, and much more dramatic. Increasing the molding temperature of the graphite fiber system to 275°C resulted in a 60% increase in strength and more than a 50% improvement in the modulus. Adding the annealing step caused further increases, nearly doubling both the strength and modulus obtained in the 190°C specimens (changes in the properties of the Thornel composites were of the same order, though slightly smaller, as those shown for the HMG materials). Oddly enough, the properties did not improve significantly until the molding temperature exceeded the 260-265°C range. In the glass fiber system, increasing the molding temperature to 275°C resulted in a 30% increase in strength and nearly doubled the tensile elongation. In contrast to the graphite, annealing of this 275°C material had little effect on the strength or modulus. Thus, there appear to be two distinct effects, one common to both the glass and graphite fibers and the other

characteristic of graphite alone. Though by no means conclusive, the property data imply that on being annealed the graphite fiber composites experienced unique internal changes which enhanced reinforcement efficiency. As indicated earlier, this is precisely the sort of change that would be expected if resin crystallization occurred on or near the fiber surface. This is further supported by the fact that the modulus increases were large, a phenomenon requiring development of oriented structures and/or crystallites within the resin itself.

Evidence for Crystallinity and Improved Wetting

The existence of a crystalline region generated around the fibers in graphite composites by annealing, as suggested by the changes in mechanical properties, has been verified. The layer is in fact quite readily seen on fibers exposed by fracture of annealed composites. Figures 1 and 2 are scanning electron micrographs of Thornel 40 fiber on the fracture surfaces of composites molded at 190°C and at 275°C with subsequent annealing at 245°C; similar results occur for the HMG system. In Figure 2 the existence of a tightly adhering layer is apparent. The micrograph in Figure 3 shows the angular character of the material on the annealed Thornel fibers more clearly.

That the material on the surface of the graphite fiber
from annealed composites is indeed oriented, if not crystalline,
polycarbonate was confirmed by transmission electron diffraction
measurements on detachment replicas of the fibers on the fracture
surfaces of annealed samples. The diffraction pattern shown in
Figure 4A exhibits discrete arcs corresponding to polycarbonate
unit-cell spacings (see schematic) which are present initially
in these measurements. The arcs disappeared rapidly when the
very low beam current was increased (see Figure 4B), even when
a cold stage was employed, indicating that the polymer melted in
the heat of the beam. It is possible, of course, that oriented
material could arise from polymer deformation during fracture,
as well as crystallization. This seems most unlikely, however,
especially in light of the very large increases in the glass
transition temperatures (Tg) of the matrix resin in the graphite
composites as compared to those of the unfilled resin and of the
glass fiber system (see Table III). An increase in Tg of this
magnitude, 10-13°C, above those of similar materials molded under
the same conditions indicates a considerable effect of the fiber
surface on the order of the resin with which it is in contact.
Comparison with the composites reinforced with graphite fibers
which are completely free of sizing agents indicated that sizing
agents are not responsible for the increases in order observed,
although the sized fibers employed here do tend to give slight-
ly stronger composites.

The decreased elongation and slightly higher modulus obtained on annealing carbosphere composites also suggest the possibility that some molecular orientation or crystallization may have occurred even though little effect on strength was observed. Figure 5, a scanning electron micrograph of the "socket" from which one of the spheres at the fracture surface has been wrenched, shows that this is the case. The tiny angular particles in the cavity seem to be relatively highly developed polycarbonate dendrites. The glass spheres in analogous composites, on the other hand, bear only occasional fragments of polymer which has wetted and adhered to the surface and leave relatively smooth cavities without any evidence of crystallinity in the resin surface.

This leaves only the property improvements achieved by molding both graphite and glass fiber composites at 275°C to be explained. As indicated by Figures 1 and 6 for the Thornel and by Figures 7 and 8 for glass, which show electron scanning micrographs of fibers at the fracture surfaces of composites processed at 190°C and 275°C respectively, this can be explained simply as a difference in wetting of the fibers by the resin. The fiber from the composite molded above the melting temperature of the resin (265°C) is completely enveloped by the resin, having been pulled out of the matrix during fracture with its coating of resin relatively intact, whereas the fiber from the composite

processed at conventional temperatures was completely denuded in pull-out. Some improvement in wetting of the glass spheres by the higher temperature processing also was observed, as noted above, but the effect was not nearly as great as in the fiber system. No explanation for the difference between the glass spheres and fibers can be offered at this time, other than to suggest that the silane size on the spheres may be involved. While found beneficial to bonding in 190° processing in earlier studies, it is possible that for some reason it impeded wetting by molten polycarbonate at the higher temperature.

The fact that better wetting appears to occur only after a critical molding temperature (260 - 265°C) is reached deserves further comment at this point. This temperature range is about where polycarbonate crystals would melt if they were present. While containing no measurable crystallinity initially, Carr, et al. (9) have shown that "amorphous" poly-carbonate is made up of the tiny 75Å balls referred to earlier. It is known that these balls generally possess uni-directional order (10) which may well be destroyed at 260-275°C. With the balls destroyed and the melt more randomized, wetting of the fiber surfaces should be greatly facilitated.

Hot Forming of Polycarbonate Composites

The facts that conventionally processed graphite-reinforced polycarbonate sheet is relatively ductile and that its properties can be nearly doubled by simple annealing suggest that this

material may be ideal for hot forming operations. Preliminary
evaluations in the laboratory have shown that this is indeed
the case. Graphite-filled (10 v/o of 1/8" fiber) polycarbonate
sheet formed at 190°C was rapidly reheated to 190°C and formed
under about 50 pounds of pressure between matched aluminum hand
molds into right-angle and semi-circular channel specimens. The
molds were then C-clamped and annealed at 235°C in a constant
temperature oven for 3 hours.

The specimens were tested in flexure by a method proposed
by Lavengood (17) in order to avoid shear coupling effects and
obtain an indication of breaking load in the region which had
undergone greatest deformation. Cross-sectional "L" and "C"
shaped test samples (1/2" wide) were accurately cut from the
specimens and loaded at the midpoints in such a way as to cause
flattening. Failure occurred near the point of loading.

In hindsight, it is likely that such a long period of
annealing is not really necessary and that it can be shortened
even more by exposing the clamped specimens briefly to tempera-
tures above Tm, 265°C, prior to annealing. The temperatures
used were dictated by limitations of the particular press and
oven employed. Nonetheless, the test results clearly show the
effectiveness of such an approach. Resistance to flexural load
was doubled in each case; see Table IV below. Here again is
evidence that thermal tailoring of the polycarbonate in the
region of the resin/fiber interface improves the ability of the
system to carry load.

CONCLUSIONS

Significant improvements in the strength and modulus of fiber reinforced polycarbonate composites can be achieved by increasing molding temperatures to above the melting point of the resin. In glass fiber composites improvement also is seen in the elongation to failure. In graphite fiber reinforced systems strength and modulus can be further enhanced by annealing moldings at temperatures 20-30° below the melting temperature. This results in formation adjacent to the fiber surface of a partially crystalline layer of resin through which stresses on the composite can apparently be more effectively transferred from fiber to fiber. It is analogous to use of innerlayers of intermediate modulus in thermosetting systems to improve performance

No improvement in properties was observed when glass and carbon sphere composites were subjected to similar molding temperatures and to thermal annealing. This seems to have been due in part to the fact that, in contrast to the fiber systems, improvements in wetting were only marginal. It is likely that this could be overcome, especially with the glass spheres, by heat cleaning prior to molding. Resin crystallization did occur in the region immediately surrounding the carbospheres, but had little effect on composite properties, perhaps because of the random dendritic nature of the crystallites with attendant formation of small voids.

The practical implications of these experiments are threefold. Use of higher processing temperatures to improve wetting of the reinforcement by the resin certainly seems desirable for all polycarbonate composites. Addition of an annealing step in a way somewhat analogous to the heat-treating of metals also seems desirable where graphite or other fibrous reinforcing agents able to nucleate crystallization in the resin are employed. So long as crystallinity is restricted to the region immediately surrounding the resin, marked improvements in composite strength are possible. Finally, hot forming of graphite and carbon-reinforced polycarbonate composites between the processing and annealing steps appears to offer particular advantages. It takes advantage of the higher processability of the unannealed material while developing higher strength and stiffness in the molded article.

ACKNOWLEDGEMENT

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TABLE I

Amorphous Thermoplastics Exhibiting
Modular Microstructure

Thermoplastic	Investigators
Polycarbonate	Carr, Geil and Baer (9)
Polyethylene Terephthalate	Yeh and Geil (10)
Polysulfone	Yang and Kardos (11)
Polystyrene	Lambert and Yeh (12)
Polypropylene (Quenched)	Gesovich (13)
Polymethyl Methacrylate	Schoon and Teichmann (14)

TABLE II

EFFECT OF THERMAL TREATMENT ON COMPOSITE PROPERTIES

Glass Sphere Composites   (Thermal Treatment)

	190°C	275°C	275°/245°C
Tensile Strength, psi x 10^3			
Unfilled	9.0	9.0	8.9
Filled	5.2	5.4	11.2
Elongation, %			
Unfilled	5.1	5.5	4.9
Filled	1.7	2.3	1.0
Modulus, psi x 10^5			
Unfilled	3.25	3.30	3.11
Filled	5.05	5.05	5.05
Glass Transition Temperature (DTA)°C			
Unfilled	145-150	145-150	145-150
Filled	147-148	140-141	141-142

Carbosphere Composites

	190°C	275°C	275°/245°C
Tensile Strength, psi x 10^3			
Unfilled	9.0	9.1	8.9
Filled	4.9	5.4	4.3
Elongation, %			
Unfilled	5.05	5.3	4.85
Filled	2.3	1.7	1.2
Modulus, psi x 10^5			
Unfilled	3.25	3.30	3.11
Filled	3.80	3.82	4.04
Glass Transition Temperature (DTA), °C			
Unfilled	145-150	145-150	145-150
Filled	143-146	143-144	140-144

TABLE III

EFFECT OF THERMAL TREATMENT ON COMPOSITE PROPERTIES

Glass Fiber Composites

(Thermal Treatment)

	190°C	275°C	275°/245°C
Tensile Strength, psi x 10^3			
Unfilled	9.0	9.1	8.9
Filled	7.6	11.1	11.2
Elongation, %			
Unfilled	5.1	5.3	4.9
Filled	1.3	2.0	2.3
Modulus, psi x 10^5			
Unfilled	3.25	3.30	3.11
Filled	8.19	8.20	9.28
Glass Transition Temperature (DTA), °C			
Unfilled	145-150	145-150	145-150
Filled	147-148	143-144	145-146

Graphite Fiber (HMG) Composites

	190°C	275°C	275°/245°C
Tensile Strength, psi x 10^3			
Unfilled	8.3	8.6	8.2
Filled	8.6	13.7	16.3
Elongation, %			
Unfilled	5.1	6.2	2.8*
Filled	0.8	0.8	0.8
Modulus, psi x 10^5			
Unfilled	3.1	3.4	3.3
Filled	19.3	29.0	37.8
Glass Transition Temperature (Torsion Pendulum), °C			
Unfilled	150	150	150
Filled	164	162	164

*Some crazing observed in this series of specimens.

TABLE IV

FLEXURAL LOADING OF HOT FORMED POLYCARBONATE COMPOSITES

	Flexural Load to Break (Pounds Force*)	
Composites Molded at 190°C	Half Cylinder	90° Channel
Unfilled	30-40	20-30
Filled (10%)	15-30	20-35
Composites Molded at 190°C and Annealed at 235°C		
Unfilled	**	**
Filled (10%)	46-62	54-64

*Range of breaking loads observed

**Excessive creep prevented annealing of unfilled specimens

FIGURE 1
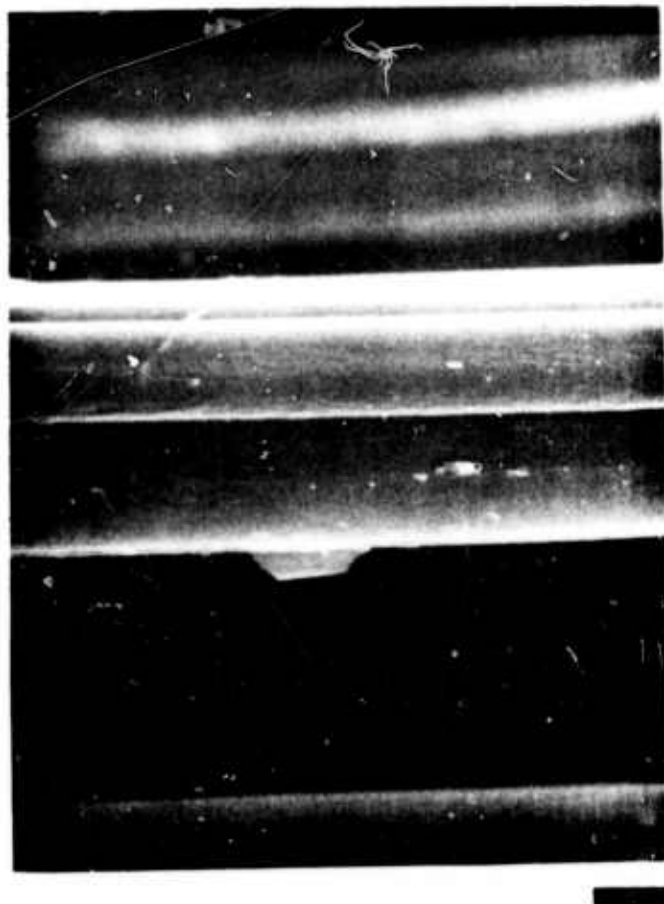
Scanning electron micrograph of
exposed Thornel fiber on the tensile
fracture surface of a sample molded
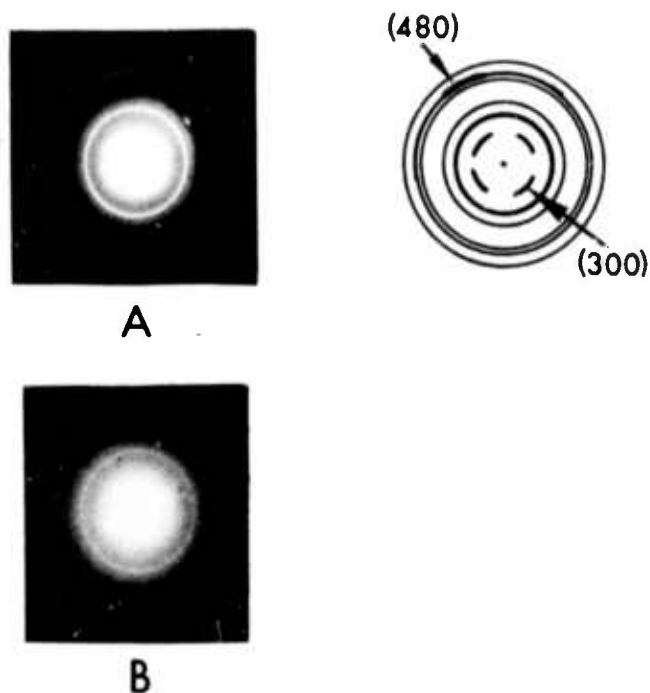at 190°C.   Scale bar represents 2
microns.

FIGURE 2
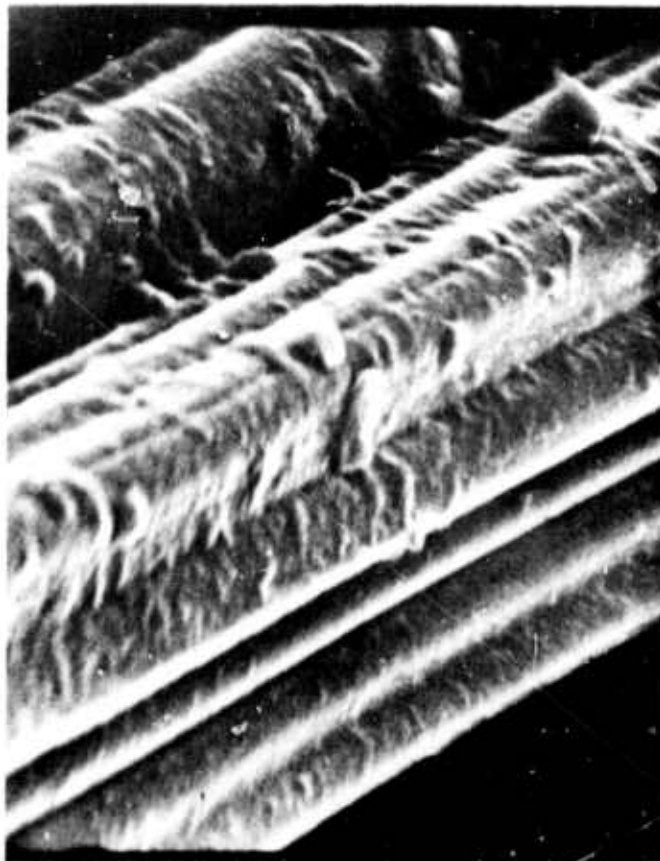
Scanning electron micrograph of
exposed Thornel fiber on the tensile
fracture surface of a sample molded
at 275°C and then annealed at 245°C
for three hours. Note the coating
of matrix which almost completely
covers the fiber. Scale bar repre-
sents 2 microns.

FIGURE 3

High magnification scanning electron
micrograph of a Thornel fiber sur-
face in the annealed sample. The
adhering polymer particles appear
to have an angular morphology
characteristic of polymer crystals.
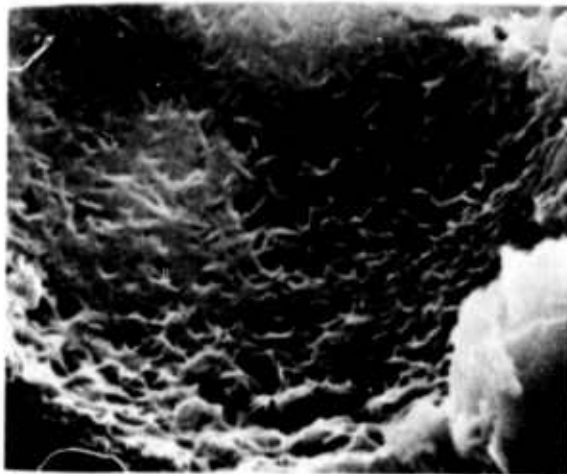Scale bar indicates 1 micron.

FIGURE 4

A

B

(480)
(300)

Diffraction patterns from a detach-
ment replica of unsized Hercules/
polycarbonate composite molded at
275°C and then annealed at 245°C
for three hours, Pt. shadowed: (A)
before electron beam heating, (B)
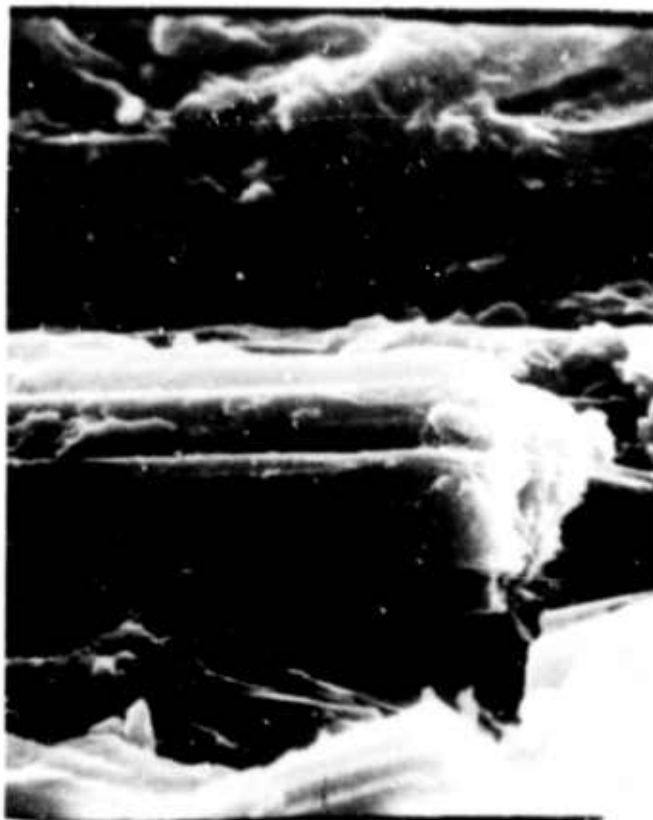after electron beam heating.

FIGURE 5

Empty socket left by a smooth
carbon sphere on the fracture
surface of a 245°C annealed
carbon/polycarbonate composite.
Polycarbonate dendrites appear
to be well developed at the
interface. Scale bar represents
2 microns.

FIGURE 6

Fracture Surface of a Polycarbonate - glass fiber composite molded at 190°C, 1800X.

FIGURE 7

Scanning electron micrograph of
exposed Thornel fiber on the tensile
fracture surface of a sample molded
at 275°C. Note the increase in
adhering matrix on the fiber over
that seen in Figure 1. Scale bar
represents 2 microns.

FIGURE 8

Scanning electron micrograph of
tensile fracture surface of an
E-glass fiber/polycarbonate com-
posite molded at 190°C. Note the
void around the fiber caused by
poor wetting. Scale bar repre-
sents 5 microns.

Fracture surface of a Polycarbonate - glass fiber
Composite molded at 275°C, with subsequent annealing at
245°C for 3 hours, 1800X